An Isotopic Dilution Approach for Quantifying Mercury Lability in Soils

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Supporting Information:

S.1. Materials and Methods:

S.1.1. Soil sampling and chemical characterisation

Soil samples were collected from nine different sites (located in some residential areas of Visp (46° 17′ 32′′ N, 7° 52′ 58′′ E) and Raron (46° 18′ 36′′ N, 7° 48′′ E) towns, Canton Valais, Switzerland, where a past industrial contamination with Hg is suspected. Three topsoil cores (collected at 0-10 cm depth) were taken from each plot within an area of 10 x 10 m or along a line-transect. One of these locations (VS2) was taken as a background reference based on a previous investigation performed by Arcadis AG at this site (mixed samples n=16) which showed THg concentrations of < 0.1 mg kg^{-1}. Samples were collected using a previously cleaned stainless steel auger and sealed in polyethylene bags for transport. Soils were air-died then sieved to < 2mm particle size for analysis.

Soil pH was measured using a glass electrode after 5 g of 2 mm sieved soils were equilibrated (end over end shaker) for 30 min in 12.5 mL of Milli-Q water. Soil organic carbon content (%SOC) and organic nitrogen were determined by a Lyco CN 628 analyser. About 0.25 g of ball milled soils were weighted into tin capsules and combusted at 1000°C. Carbon was measured by an infrared detector in oxygen rich environment while nitrogen was measured by thermal conductivity in helium. Reactive Fe, Al and Mn oxides is soils were extracted by the dithionite procedure developed by Kostka and Luther [1]. Finely ground soils (agate ball mill) were suspended in 25 mL of a solution containing 0.22 M tri-sodium citrate, 0.11 M sodium hydrogen carbonate and 0.1 M sodium dithionite and shaken for 16 hours in a water bath at 40°C. Centrifuged and filtered samples were retained for analysis of Fe, Al, and Mn by ICP-OES and concentrations (mg kg^{-1}) of Fe_2O_3, MnO_2, and $Al(OH)_3$ were calculated. Concentrations of metals in the dithionite and acid extracts (diluted in 5% v/v HNO_3) were assayed by an Agilent ICP-OES 5100. Sample processing was undertaken using ICP Expert software (version 7.2). Total sulfur in soil samples was extracted by the Swiss standard regulations on soil pollution protocol (Verordnung über Belastungen des Bodens; VBBo) [2]. In triplicates, 10 g of 2mm sieved

soils were extracted with 100 mL 2M analytical grade HNO_3 in a boiling water bath for 120 min. Total sulfur in the acid extracts was also assayed by ICP-OES. Total soil mercury (THg) was measured using a Perkin Elmer SMS100 atomic absorption spectrometer according to the EPA standard method 7473. Soil samples were thermally decomposed at 750°C followed by amalgamation on a gold-trap and then analysis of Hg cold vapors. Certified reference lake sediment material (IAEA SL-1) was used for calibration. Replicate samples and reference material were analyzed regularly (10% of the sampling sequence) and the precision was under 10% relative standard deviation (SD).

S.1.2. Determination of isotopically exchangeable Hg (Hg_E) in soil

Hamon, et al. [3] and Marzouk, et al. [4] demonstrated that the spiked isotopes may disturb the natural isotopic equilibrium leading to a systematic variation in the measured E-values at higher spike levels. However, in practice, the amount of the added spike varied from c. 5% to 400% of the metal soil concentration and the 'appropriate' spike concentrations were usually selected based on the investigated metal, its concentration, soil properties and the robustness and accuracy of the isotopic ratio measurement [4-15].

In this work, spike levels were chosen based on a preliminary experiment involving 3 soils with high, medium and low THg contents which showed that at least 50% increase in the soil ^{199}Hg and ^{196}Hg content was required for robust isotopic ratio (IR) measurements. This was mainly due to our carryover elimination strategy (SI, S.1.3), which included diluting all solutions to < 2 $\mu g\ L^{-1}$ Hg. Therefore, a careful balance was required between maintaining analytical precision while keeping spike concentrations to the minimum to avoid possible perturbation of the natural equilibrium [3, 7]. The original plan was not to exceed 100% of soil ^{196}Hg or ^{199}Hg; however, this was impractical for ^{196}Hg in all soils due to its very low natural abundance. The authenticity of the estimated values of HgE was determined by checking their consistency against different spike levels [3, 4, 16]. The possible precipitation of Hg isotopes at high spike concentrations was modelled with Visual MINTEQ 3.1 for the highest spike level in our range (4.1 $\mu g\ mL^{-1}$ ^{199}Hg). Results showed that, under

our experimental conditions, both $Hg(OH)_2$ and $HgCl_2$ displayed negative saturation indexes (-7.4 and -1.2, respectively) indicating negligible precipitation.

S.1.3. Measuring equilibrium Hg isotopic abundances

Isotopic abundances of ^{196}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg and ^{202}Hg in both spiked and un-spiked samples were assayed by an Agilent 7700x ICP-MS in helium collision mode. A three steps washing sequence between samples was used to eliminate memory effect and cross contamination; this included (i) a solution of 1 g L^{-1} EDTA, 0.08 g L^{-1} Triton X-100 and 6 g L^{-1} NH_4OH, (ii) technical grade 5% HNO_3/HCl and (iii) the matrix solution (ultra-pure 1% HNO_3/ 0.5% HCl). In addition, all samples and standards were diluted to a 0.05 - 2 μg L^{-1} range of total Hg.

For internal mass bias correction, Tl solution (10 μg L^{-1}), in a matrix of ultra-pure 1% HNO_3 and 0.5% HCl, was introduced in the internal standard line via a T-piece and the variation in the $^{203}Tl/^{205}Tl$ ratios was used to correct shifts in Hg isotopic ratios [6, 17, 18]. Moreover, external mass discrimination correction was applied by repeatedly analyzing a 2 μg L^{-1} Hg ICP-MS standard every three samples [19]. Changes in the measured count rate (CPS) ratios of the bracketing Hg standard were applied by linear extrapolation to the intervening samples [5, 11].

The abundance of ^{195}Pt was measured to monitor and correct for possible isobaric interference between ^{196}Pt and ^{196}Hg although in practice Pt concentrations were below detection limits in all samples.

To ensure high level of measurement precision, repeated runs of very short quadrupole dwell times were applied. Five runs, each composed of 1000 sweeps, were applied to each sample and the dwell times were 5.01 ms for ^{195}Pt, ^{196}Hg, ^{199}Hg, ^{200}Hg, ^{201}Hg, ^{202}Hg, ^{203}Tl and ^{205}Tl. RSDs between the measured counts per second (CPS) of the five runs, for each isotope, were always kept below 1%; data were rejected and repeated if RSD exceeded 1% for any single isotope in the sequence. To allow for the fast jumping quadrupole to

settle locally before sweeping through the main isotopes [4], ^{194}Pt (0.3 ms) was also added to the sequence to work as a resting mass.

S.1.4. E-value comparison with extraction methods

Despite the popularity of extraction methods to estimate the available fraction of soil Hg, unfortunately there is no universal protocol available such as the sequential extraction procedure developed by Tessier, et al. [20] for classic hard metals [21]. The type and sequence of the selected extractants have always been an empirical decision depending on the nature of soil or the targeted Hg species [21, 22]. Moreover, when compared to Hg uptake by flora or fauna, good correlations have been observed between bioavailable Hg and Hg from all soil fractions indicating that labile Hg is not exclusively bound to specific soil phases [23, 24]. However, the first step of extraction using ammonium acetate or magnesium chloride to extract 'exchangeable Hg' was common in the available literature [21, 22, 25-27].

For comparison with Hg E-value, 'Exchangeable' mercury in all soil samples was extracted by ammonium acetate or magnesium chloride as described by Han, et al. [25] and Panyametheekul [26]. In duplicates, 2 g of <2mm sieved soils were suspended in 30 mL 1 M ammonium acetate or 0.5 M magnesium chloride and shaken for 1 h and 2 h, respectively, at room temperature. Centrifuged and filtered samples were diluted with 5 % HCl as necessary and Hg concentrations were measured by an Agilent ICP-OES 5100 fitted with Multimode Sample Introduction System (MSIS) for vapour generation.

S.2. Results and Discussion:

S.2.1. Soil Properties

Key soil parameters including total soil Hg (THg), pH, soil organic carbon (Org-C), total nitrogen, total S, reactive Fe, Mn and Al oxides are summarized by sampling site in Table S1. All soils were alkaline or slightly acidic with a mean pH range of 6.2 to 8.2. In general, soils showed average organic carbon content (2.6 to 4.5 %). Total soil Hg ranged in average from 0.37 to 310 mg kg^{-1}. All locations showed THg concentrations higher than the 0.37 mg kg^{-1} measured in the VS2 background (reference) site. However, THg

138 concentrations were noticeably elevated (230 - 390 mg kg^{-1}) in location VS2 followed by
139 location TT2 indicating high levels of mercury contamination.

Table S1. Soil properties by sampling locations including total Hg (THg), pH, organic carbon (org-C), N, total S and reactive metal oxides in soils in Visp and Raron, Switzerland differently contaminated by Hg. SD= standard deviation.

Site	*THg (mg kg^{-1})*		*pH*		*Org-C (%)*		*N (%)*		*S (%)*		*Al(OH)$_3$ (g kg^{-1})*		*MnO$_2$ (g kg^{-1})*		*Fe$_2$O$_3$ (g kg^{-1})*	
	Mean	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*	*Mean*	*SD*
HW1	0.95	0.95	7.29	0.05	2.63	0.31	0.21	0.02	0.36	0.03	0.72	0.16	0.23	0.04	4.00	0.67
HK1	2.80	1.21	6.82	0.52	3.43	0.22	0.31	0.05	0.47	0.06	0.47	0.12	0.13	0.05	3.40	0.74
HK2	2.73	0.25	7.61	0.15	2.95	0.54	0.21	0.05	0.35	0.08	0.43	0.03	0.18	0.02	3.84	0.31
XX1	7.54	3.45	7.36	0.14	4.07	0.30	0.40	0.03	0.63	0.05	0.45	0.05	0.14	0.04	2.91	0.40
XX2	16.9	7.86	7.33	0.38	4.48	0.81	0.47	0.07	0.71	0.05	0.55	0.01	0.19	0.01	4.12	0.26
TT1	2.68	1.63	7.48	0.27	3.89	0.67	0.31	0.03	0.56	0.09	0.42	0.10	0.21	0.16	3.96	0.73
TT2	38.1	8.62	8.20	0.13	2.95	0.12	0.23	0.01	0.78	0.16	0.62	0.01	0.16	0.01	3.82	0.20
VS1	310	80	7.26	0.22	3.49	1.33	0.24	0.15	0.54	0.22	0.70	0.20	0.16	0.06	3.44	0.88
VS2	0.37	0.29	6.20	0.51	3.03	0.96	0.29	0.10	0.42	0.16	0.40	0.04	0.14	0.01	2.85	0.29

Table S2. Mass bias correction factors in the ratios of spike isotopes (^{196}Hg and ^{199}Hg) to reference isotopes (^{200}Hg, ^{201}Hg and ^{202}Hg). The expected drift due to mass discrimination was corrected for by periodically running a 2 μg L^{-1} certified Hg standard and applying the changes in its isotopic ratios to the intervening samples. A, B and C are different soil sampled from the same location while 1 and 2 are replicates of the same soil. Isotopic ratios of the bracketing Hg standard used for mass bias correction are displayed in bold italic font in their exact position in the analysis sequence.

Location	Soil	Spiked Sample	Isotopic ratios mass bias correction factors					
			^{196}Hg/^{200}Hg	^{196}Hg/^{201}Hg	^{196}Hg/^{202}Hg	^{199}Hg/^{200}Hg	^{199}Hg/^{201}Hg	^{199}Hg/^{202}Hg
	Natural Ratio		*0.006494*	*0.011381*	*0.005023*	*0.730303*	*1.279970*	*0.564970*
		Hg std.	*0.006748*	*0.011737*	*0.00518*	*0.727679*	*1.265749*	*0.558636*
HW1	A	1	0.928	0.930	0.926	1.000	1.002	0.998
		2	0.910	0.911	0.907	1.001	1.002	0.997
	B	1	0.892	0.892	0.888	1.001	1.002	0.997
		Hg std.	*0.007287*	*0.01271*	*0.005611*	*0.725363*	*1.265201*	*0.558526*
		2	0.882	0.882	0.877	1.001	1.001	0.996
	C	1	0.891	0.891	0.885	1.000	1.000	0.994
		2	0.899	0.899	0.894	0.999	0.999	0.993
		Hg std.	*0.00697*	*0.012133*	*0.005354*	*0.726552*	*1.264826*	*0.55813*
HK1	A	1	0.886	0.886	0.880	0.999	0.999	0.993
		2	0.864	0.864	0.859	0.999	0.998	0.993
	B	1	0.843	0.842	0.838	0.999	0.998	0.994
		Hg std.	*0.007735*	*0.013497*	*0.00595*	*0.726829*	*1.26825*	*0.559124*
		2	0.825	0.825	0.821	0.999	0.999	0.994
	C	1	0.829	0.830	0.825	0.999	1.000	0.995
		2	0.833	0.834	0.829	1.000	1.001	0.995
		Hg std.	*0.00759*	*0.013194*	*0.005839*	*0.727214*	*1.264063*	*0.55947*
HK2	A	1	0.839	0.842	0.836	1.000	1.003	0.997
		2	0.838	0.841	0.835	1.000	1.003	0.997
	B	1	0.837	0.839	0.835	1.000	1.003	0.998
		Hg std.	*0.007637*	*0.013286*	*0.005867*	*0.727007*	*1.264733*	*0.558483*
		2	0.834	0.836	0.832	1.000	1.002	0.997
	C	1	0.833	0.834	0.830	1.000	1.001	0.996
		2	0.832	0.832	0.829	0.999	1.000	0.996
		Hg std.	*0.007662*	*0.013364*	*0.005892*	*0.727356*	*1.268739*	*0.55934*
XX1	A	1	0.818	0.818	0.815	0.999	0.999	0.995
		2	0.806	0.807	0.803	1.000	1.000	0.995
	B	1	0.794	0.795	0.790	1.000	1.000	0.995
		Hg std.	*0.008135*	*0.014177*	*0.006264*	*0.726427*	*1.266029*	*0.559366*
		2	0.764	0.765	0.761	0.999	1.000	0.994
	C	1	0.746	0.747	0.743	0.998	0.999	0.994
		2	0.728	0.729	0.726	0.997	0.998	0.993
		Hg std.	*0.007726*	*0.013443*	*0.005942*	*0.727105*	*1.265086*	*0.559147*
XX2	A	1	0.818	0.819	0.816	1.002	1.003	0.998
		2	0.781	0.782	0.778	1.001	1.003	0.997
	B	1	0.743	0.745	0.740	1.000	1.002	0.996
		Hg std.	*0.007802*	*0.013552*	*0.00599*	*0.728428*	*1.265264*	*0.559249*
		2	0.713	0.715	0.710	0.999	1.001	0.994

	C	1	0.722	0.722	0.718	0.999	1.000	0.994
		2	0.730	0.730	0.726	0.999	0.999	0.993
		Hg std.	*0.00754*	*0.013134*	*0.005797*	*0.726265*	*1.265067*	*0.558402*
TT1	A	1	0.833	0.835	0.831	1.001	1.002	0.998
		2	0.819	0.819	0.816	1.000	1.000	0.996
	B	1	0.804	0.804	0.801	0.999	0.998	0.994
		Hg std.	*0.008032*	*0.014019*	*0.006174*	*0.727854*	*1.27036*	*0.559462*
		2	0.795	0.794	0.791	0.998	0.998	0.994
	C	1	0.799	0.800	0.796	0.998	0.999	0.995
		2	0.804	0.806	0.802	0.999	1.001	0.996
		Hg std.	*0.007456*	*0.013006*	*0.005741*	*0.725003*	*1.264739*	*0.558205*
TT2	A	1	0.817	0.818	0.812	0.997	0.999	0.991
		2	0.816	0.817	0.811	0.997	0.999	0.991
	B	1	0.814	0.816	0.810	0.997	0.999	0.992
		Hg std.	*0.009027*	*0.015686*	*0.006937*	*0.727826*	*1.264719*	*0.559305*
		2	0.910	0.910	0.907	1.001	1.001	0.998
	C	1	0.889	0.890	0.887	1.001	1.002	0.999
		2	0.869	0.870	0.867	1.001	1.003	0.999
		Hg std.	*0.008595*	*0.015009*	*0.006621*	*0.72658*	*1.268736*	*0.559692*
VS1	A	1	0.751	0.750	0.746	0.999	0.998	0.993
		2	0.763	0.762	0.758	0.999	0.999	0.993
	B	1	0.775	0.775	0.770	0.999	0.999	0.993
		Hg std.	*0.008069*	*0.01405*	*0.006207*	*0.726986*	*1.265819*	*0.559237*
		2	0.729	0.730	0.725	0.997	0.998	0.991
	C	1	0.671	0.672	0.667	0.995	0.997	0.989
		2	0.614	0.615	0.610	0.994	0.995	0.987
		Hg std.	*0.011371*	*0.01976*	*0.008739*	*0.731391*	*1.270962*	*0.562087*

Table S3. E-values of Hg (mg kg^{-1}), for all collected samples, as calculated by equation 1 using ^{199}Hg as spike isotope and ^{200}Hg, ^{201}Hg or ^{202}Hg as reference isotopes. A, B and C represent different samples collected from the same location. Standard errors are displayed between brackets (two spiked and two un-spiked replicates).

Location	Sample	E-Value ($^{199}Hg/^{200}Hg$)	E-Value ($^{199}Hg/^{201}Hg$)	E-Value ($^{199}Hg/^{202}Hg$)
HW1	A	0.16 (0.00)	0.15 (0.00)	0.16 (0.00)
	B	0.07 (0.02)	0.06 (0.01)	0.06 (0.01)
	C	0.08 (0.01)	0.07 (0.00)	0.08 (0.01)
HK1	A	0.41 (0.02)	0.36 (0.03)	0.42 (0.01)
	B	0.54 (0.06)	0.52 (0.09)	0.55 (0.08)
	C	0.14 (0.00)	0.13 (0.00)	0.14 (0.00)
HK2	A	0.62 (0.05)	0.57 (0.05)	0.61 (0.05)
	B	0.72 (0.03)	0.71 (0.25)	0.72 (0.14)
	C	0.64 (0.03)	0.61 (0.02)	0.65 (0.01)
XX1	A	0.56 (0.03)	0.54 (0.04)	0.59 (0.04)
	B	1.29 (0.02)	1.18 (0.04)	1.29 (0.01)
	C	1.08 (0.05)	1.01 (0.04)	1.09 (0.02)
XX2	A	1.69 (0.04)	1.59 (0.05)	1.69 (0.04)
	B	1.66 (0.23)	1.54 (0.15)	1.67 (0.05)
	C	4.91 (0.25)	4.70 (0.08)	4.95 (0.16)
TT1	A	0.78 (0.17)	0.75 (0.18)	0.78 (0.17)
	B	0.12 (0.01)	0.11 (0.02)	0.12 (0.01)
	C	0.35 (0.03)	0.32 (0.15)	0.36 (0.05)
TT2	A	5.99 (0.13)	5.80 (0.11)	5.99 (0.17)
	B	5.42 (0.17)	5.36 (0.48)	5.46 (0.25)
	C	6.83 (0.04)	6.69 (0.14)	6.85 (0.06)
VS1	A	131(16.8)	131 (16.7)	132 (15.9)
	B	74.9 (0.28)	73.7 (1.09)	75.9 (0.65)
	C	43.7 (2.69)	43.3 (3.01)	44.0 (1.89)

Table S4. Mercury lability (%HgE), for all samples, calculated by equation 1, against different ^{199}Hg spike to natural ratios. A, B and C are different samples from the same location. Standard errors are displayed between brackets for two spiked (for each spike level) and two un-spiked replicates.

Location	Sample	Hg Lability (%HgE)		
Spike / Native ^{199}Hg		*50 %*	*100 %*	*200 %*
HW1	A	7.82 (0.01)	7.76 (0.14)	7.81 (0.12)
	B	16.5 (3.65)	16.2 (3.45)	16.2 (3.48)
	C	19.8 (2.34)	20.2 (2.23)	20.1 (2.2)
HK1	A	11.7 (0.42)	12 (0.18)	12 (0.18)
	B	15.5 (1.78)	15.7 (2.24)	15.7 (2.24)
	C	10.1 (0.25)	10.2 (0.13)	10.1 (0.16)
HK2	A	22.8 (1.82)	22.5 (2.01)	22.6 (1.92)
	B	24.1 (4.32)	24.1 (4.54)	24.2 (4.5)
	C	25.5 (1.29)	26 (1.17)	26 (1.11)
XX1	A	16.5 (0.88)	16.3 (1.02)	16.4 (1)
	B	14.6 (0.43)	14.7 (0.57)	14.7 (0.57)
	C	10.6 (0.26)	10.7 (0.15)	10.7 (0.13)
XX2	A	14.1 (0.28)	14.1 (0.3)	14.2 (0.29)
	B	13 (0.26)	13.1 (0.42)	13.1 (0.41)
	C	18.9 (0.59)	19 (0.61)	19.1 (0.6)
TT1	A	18 (3.80)	18 (3.89)	17.9 (3.84)
	B	10.7 (1.26)	10.8 (1.23)	10.7 (1.29)
	C	13.5 (1.63)	13.7 (1.73)	13.7 (1.79)
TT2	A	15.5 (0.33)	15.4 (0.43)	15.6 (0.43)
	B	18.6 (0.93)	18.8 (0.85)	18.7 (0.83)
	C	14.8 (0.99)	14.8 (0.09)	14.8 (0.13)
VS1	A	33.6 (4.23)	33.8 (4.07)	33.6 (3.84)
	B	24.2 (0.08)	24.5 (0.21)	24.5 (0.19)
	C	19 (1.15)	19.1 (1.17)	19.1 (1.12)
VS2	A	27.5 (2.16)	27.1 (1.78)	27 (1.85)
	B	46 (8.31)	45.9 (8.07)	45.8 (8.15)
	C	15.3 (0.64)	15.1 (0.61)	15.1 (0.64)

Table S5. Pearson correlation coefficients of Hg labile pool (HgE; mg kg^{-1}) and Hg lability (%HgE) with soil parameters in all soils (n=27).

Soil Parameter	Pearson Correlation (r) with HgE (mg kg^{-1})	Pearson Correlation (r) with %HgE
THg	0.98	0.63
pH	-0.07	0.14
N	-0.13	-0.26
Org-C	0.11	-0.03
S	0.11	-0.04
$Al(OH)_3$	0.47	0.08
MnO_2	-0.06	-0.17
Fe_2O_3	-0.03	0.00

Table S6. Linear stepwise regression (Minitab 17) coefficients and P-values. Labile Hg (HgE; mg kg^{-1}) and Hg lability (%HgE) parameterised by all other soil parameters including THg, pH, N, Org-C, S and Al, Mn and Fe oxides.

	HgE (mg kg^{-1})		%HgE	
Regression	R^2 = 0.96		R^2 = 0.63	
	Coefficients	P-value	Coefficients	P-value
Intercept	-4.98	0.90	-4.70	0.83
THg	0.27	0.00	0.05	0.01
pH	-1.92	0.73	2.70	0.39
N	-46.2	0.47	1.85	0.96
Org-C	7.57	0.32	-0.52	0.90
S	0.00	0.85	0.00	0.45
$Al(OH)_3$	2.89	0.88	-20.5	0.08
MnO_2	-1.44	0.98	-34.4	0.20
Fe_2O_3	1.58	0.77	5.85	0.07

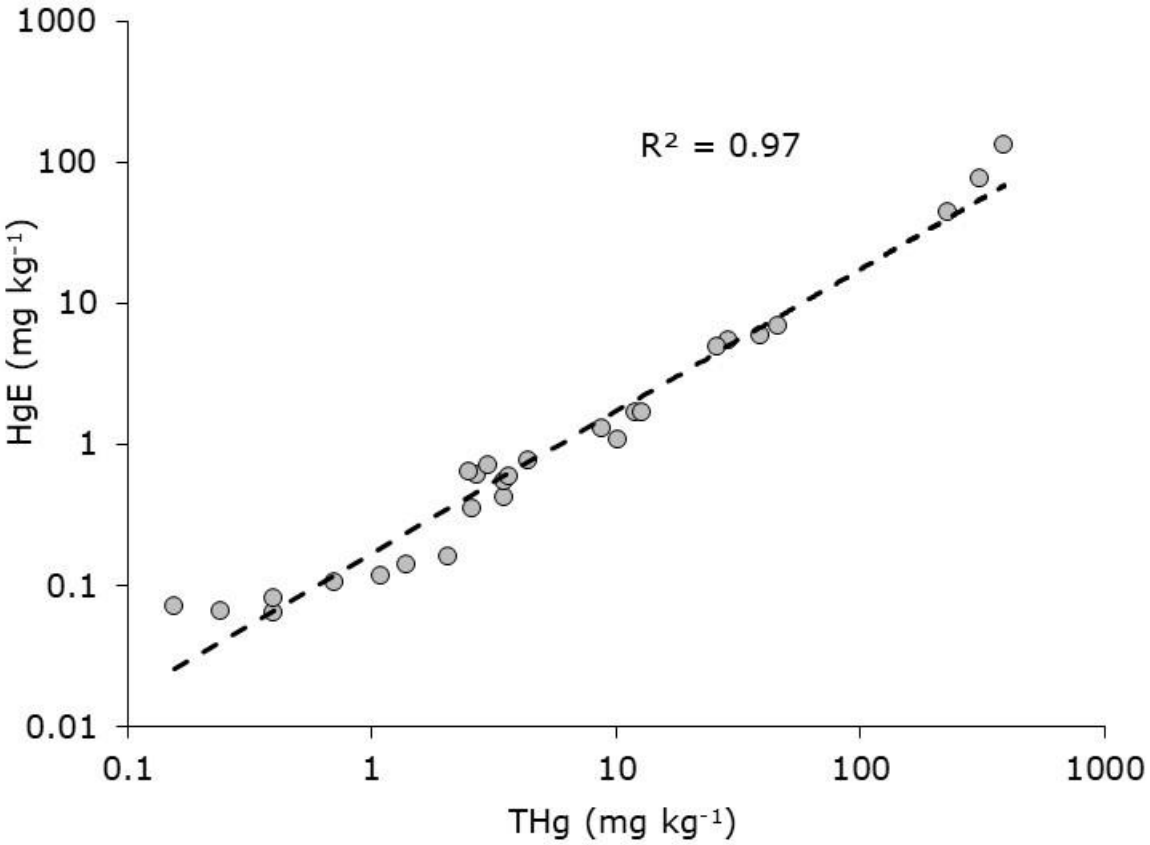

Figure S1. Total soil mercury (THg) (mg kg^{-1}) plotted against corresponding labile Hg (HgE; mg kg^{-1}) for all data points (n=27). The dashed line represents a 'power' relationship between x and y parameters.

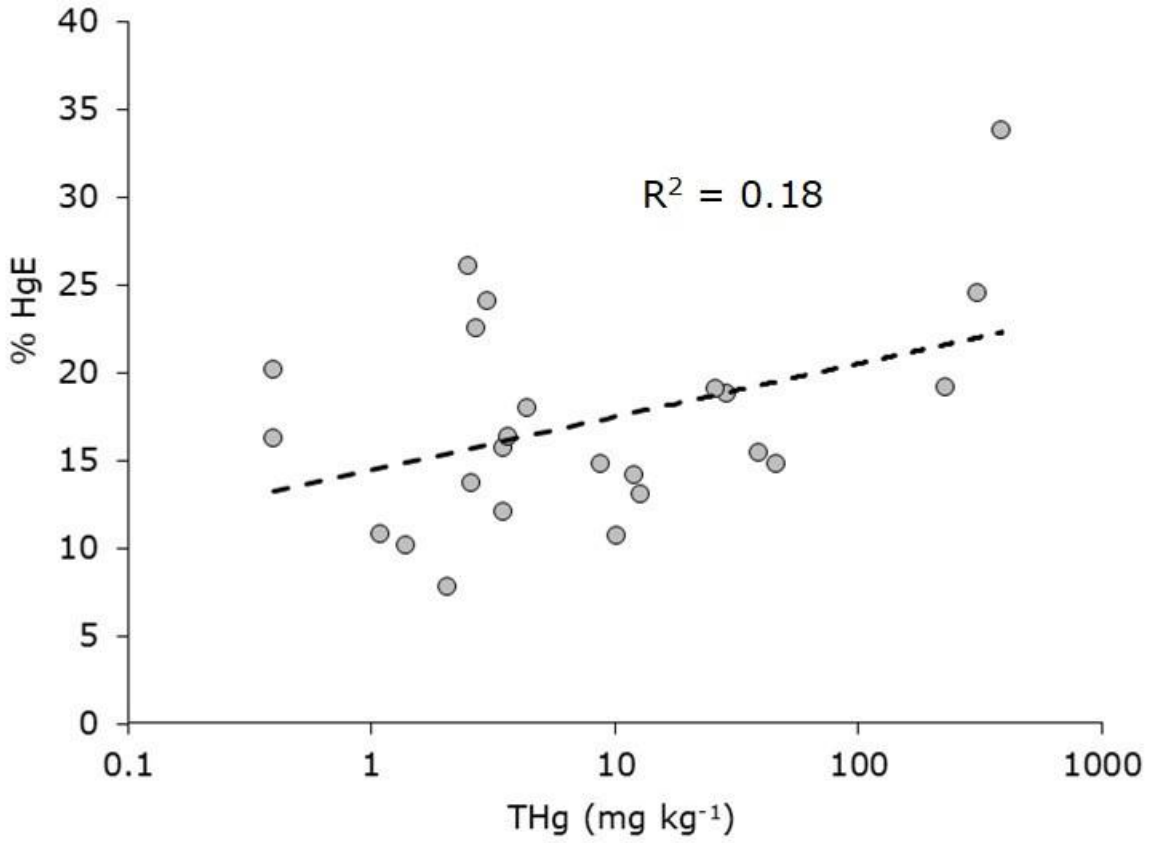

Figure S2. Total soil mercury (THg) (mg kg^{-1}) plotted against Hg lability (%HgE) for all data points (n=27). The dashed line represents a 'logarithmic' relationship between x and y parameters.

Reference

1. Kostka, J. E.; Luther, G. W., Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta* **1994,** *58*, (7), 1701-1710.
2. Bundesrat, S., Verordnung über Belastungen des Bodens (VBBo). 814.12, 01.07. 1998. *Bern, Schweiz* **1998**.
3. Hamon, R. E.; Parker, D. R.; Lombi, E., Advances in isotopic dilution techniques in trace element research: a review of methodologies, benefits, and limitations. *Advances in agronomy* **2008,** *99*, 289-343.
4. Marzouk, E. R.; Chenery, S. R.; Young, S. D., Measuring reactive metal in soil: a comparison of multi-element isotopic dilution and chemical extraction. *European Journal of Soil Science* **2013,** *64*, (4), 526-536.
5. Atkinson, N. R.; Bailey, E. H.; Tye, A. M.; Breward, N.; Young, S. D., Fractionation of lead in soil by isotopic dilution and sequential extraction. *Environmental Chemistry* **2011,** *8*, (5), 493-500.
6. Chenery, S. R.; Izquierdo, M.; Marzouk, E.; Klinck, B.; Palumbo-Roe, B.; Tye, A. M., Soil-plant interactions and the uptake of Pb at abandoned mining sites in the Rookhope catchment of the N. Pennines, UK - A Pb isotope study. *Science of the Total Environment* **2012,** *433*, 547-560.
7. Gabler, H. E.; Bahr, A.; Heidkamp, A.; Utermann, J., Enriched stable isotopes for determining the isotopically exchangeable element content in soils. *European Journal of Soil Science* **2007,** *58*, (3), 746-757.
8. Garforth, J. M.; Bailey, E. H.; Tye, A. M.; Young, S. D.; Lofts, S., Using isotopic dilution to assess chemical extraction of labile Ni, Cu, Zn, Cd and Pb in soils. *Chemosphere* **2016,** *155*, 534-541.
9. Izquierdo, M.; Tye, A.; Chenery, S., Sources, lability and solubility of Pb in alluvial soils of the River Trent catchment, UK. *Science of the Total Environment* **2012,** *433*, 110-122.
10. Mao, L. C.; Bailey, E. H.; Chester, J.; Dean, J.; Ander, E. L.; Chenery, S. R.; Young, S. D., Lability of Pb in soil: effects of soil properties and contaminant source. *Environmental Chemistry* **2014,** *11*, (6), 690-701.
11. Marzouk, E. R.; Chenery, S. R.; Young, S. D., Predicting the solubility and lability of Zn, Cd, and Pb in soils from a minespoil-contaminated catchment by stable isotopic exchange. *Geochimica Et Cosmochimica Acta* **2013,** *123*, 1-16.
12. Nolan, A. L.; Ma, Y. B.; Lombi, E.; McLaughlin, M. J., Measurement of labile Cu in soil using stable isotope dilution and isotope ratio analysis by ICP-MS. *Analytical and Bioanalytical Chemistry* **2004,** *380*, (5-6), 789-797.
13. Sivry, Y.; Riotte, J.; Munoz, M.; Sappin-Didier, V.; Dupre, B., Study of labile Cd pool in contaminated soil using stable isotope analysis, radioactive isotope dilution and sequential extraction. *Geochimica Et Cosmochimica Acta* **2006,** *70*, (18), A594-A594.
14. Tongtavee, N.; Shiowatana, J.; McLaren, R. G.; Gray, C. W., Assessment of lead availability in contaminated soil using isotope dilution techniques. *Science of the Total Environment* **2005,** *348*, (1-3), 244-256.
15. Young, S. D.; Tye, A.; Carstensen, A.; Resende, L.; Crout, N., Methods for determining labile cadmium and zinc in soil. *European Journal of Soil Science* **2000,** *51*, (1), 129-136.
16. Sterckeman, T.; Carignan, J.; Srayeddin, I.; Baize, D.; Cloquet, C., Availability of soil cadmium using stable and radioactive isotope dilution. *Geoderma* **2009,** *153*, (3), 372-378.
17. Blum, J. D.; Bergquist, B. A., Reporting of variations in the natural isotopic composition of mercury. *Analytical and Bioanalytical Chemistry* **2007,** *388*, (2), 353-359.
18. Rodríguez-Castrillón, J. Á.; Moldovan, M.; Alonso, J. I. G.; Lucena, J. J.; García-Tomé, M. L.; Hernández-Apaolaza, L., Isotope pattern deconvolution as a tool to study iron metabolism in plants. *Analytical and bioanalytical chemistry* **2008,** *390*, (2), 579-590.
19. Albarede, F.; Telouk, P.; Blichert-Toft, J.; Boyet, M.; Agranier, A.; Nelson, B., Precise and accurate isotopic measurements using multiple-collector ICPMS. *Geochimica Et Cosmochimica Acta* **2004,** *68*, (12), 2725-2744.

20. Tessier, A.; Campbell, P. G.; Bisson, M., Sequential extraction procedure for the speciation of particulate trace metals. *Analytical chemistry* **1979,** *51*, (7), 844-851.
21. Issaro, N.; Abi-Ghanem, C.; Bermond, A., Fractionation studies of mercury in soils and sediments: A review of the chemical reagents used for mercury extraction. *Analytica Chimica Acta* **2009,** *631*, (1), 1-12.
22. Reis, A. T.; Lopes, C. B.; Davidson, C. M.; Duarte, A. C.; Pereira, E., Extraction of available and labile fractions of mercury from contaminated soils: The role of operational parameters. *Geoderma* **2015,** *259*, 213-223.
23. Han, F. X.; Su, Y.; Shi, Z.; Xia, Y.; Tian, W.; Philips, V.; Monts, D. L.; Gu, M.; Liang, Y., Mercury distribution and speciation in floodplain soils and uptake into native earthworms (Diplocardia spp.). *Geoderma* **2012,** *170*, 261-268.
24. Jing, Y.; He, Z.; Yang, X.; Sun, C., Evaluation of Soil Tests for Plant-available Mercury in a Soil–Crop Rotation System. *Communications in soil science and plant analysis* **2008,** *39*, (19-20), 3032-3046.
25. Han, F. X.; Su, Y.; Monts, D. L.; Waggoner, C. A.; Plodinec, M. J., Binding, distribution, and plant uptake of mercury in a soil from Oak Ridge, Tennessee, USA. *Science of the Total Environment* **2006,** *368*, (2-3), 753-768.
26. Panyametheekul, S., An operationally defined method to determine the speciation of mercury. *Environmental Geochemistry and Health* **2004,** *26*, (1), 51-57.
27. Renneberg, A. J.; Dudas, M. J., Transformations of elemental mercury to inorganic and organic forms in mercury and hydrocarbon co-contaminated soils. *Chemosphere* **2001,** *45*, (6-7), 1103-1109.